Supplemental information

Given that air samples stored in metal have been known to sometimes have in-growth of H_2 when stored for significant periods of time, there was concern over the stability of H_2 in the canisters from the Whole Air Sampler. To investigate for this possibility, we analyzed five canister/flask sample pairs that had aliquots separated into evacuated glass flasks 14 to 15 months after initial sampling and ~ 6 months prior to isotopic analysis. Under these conditions, samples stored in canisters for the entire 20 to 21 months prior to analysis would potentially contain 40 % greater in-growth contamination than the aliquots transferred to glass flasks. With the exception of the canister from pressure altitude 18.6 km sampled on 2/3/00 (634 ppb canister compared to 502 ppb flask), no significant difference in concentration was observed between can/flask pairs. Consistent with the expectation that in-growth of H_2 would be expected to be isotopically depleted, δD values obtained from flasks were in all cases greater than those for the original canister; however, with one notable exception (Table 1, 3/11/00,pressure altitude 20.2 km, $\Delta c/f$=72 ‰) the difference between canister/flask pairs is not significantly greater than that for duplicate analyses of individual cans. Canister/flask pair results are plotted separately in Fig. 2 with the two exceptions noted above highlighted. In-growth of H_2 in a given canister would be expected to be highly random and given the coherency of the remaining data, we conclude that the data represent the true variability of δD in stratospheric H_2.

Supplemental table

Sample date	Latitude (degrees)	Longitude (degrees)	Pressure Altitude (km)	can / flask c or f	Transfer date†	δD of H_2♣ per mil	Δ_{dup}♦	$\Delta_{c/f}$♠	H_2 (MS) ppb‡	CH_4 ppb	N_2O ppb
1/6/00	21.5	-120	18.4	f	2/14/00	152	-	-	500	1672	297
1/31/00	77.8	13.4	17.9	f	7/18/00	250	-	-	497	1252	195
2/2/00	65.8	63.0	19.0	c	-	326	-	-	520	1058	141
2/2/00	76.0	15.0	16.7	c*	-	216	12	-	523	1407	234
2/2/00	70.8	18.9	20.4	c	-	364	-	-	493	914	102
2/3/00	72.8	24.7	15.7	c	-	183	-	-	587	1475	252
2/3/00	72.3	25.4	16.8	c	-	226	-	-	554	1366	224
2/3/00	71.6	26.2	18.6	c/f*	5/16/01	206	35	28	546	1158	168
2/3/00	71.4	26.4	19.7	c	-	315	-	-	515	1057	140
2/3/00	68.4	24.1	13.5	c*	-	124	10	-	489	1663	293
2/3/00	68.3	23.3-	11.4	c*/f	5/16/01	133	29	15	468	1737	308
3/7/00	80.7	50.7	19.5	c	-	399	-	-	536	888	96
3/7/00	81.1	25.7	16.5	c/f	5/13/01	247	-	25	459	1305	208
3/11/00	70.1	29.3	20.1	c*	-	438	8	-	508	719	53
3/11/00	71.9	29.8	20.2	c*/f	5/15/01	356	1	72	531	716	52
3/11/00	73.5	27.3	20.4	c/f	5/15/01	403	-	22	460	733	57
3/12/00	78.9	41.7	18.3	c*	-	316	1	-	493	1099	152
3/12/00	79.1	37.2	19.1	c	-	336	-	-	550	999	125
3/12/00	79.4	26.8	19.6	c	-	397	-	-	608	854	87
3/12/00	79.0	6.8	19.7	f	7/25/00	386	-	-	418	790	70
3/12/00	77.5	8.3	19.8	c	-	378	-	-	563	798	72
3/16/00	67.4	13.6	16.8	c	-	161	-	-	534	1614	284

All samples analyzed for H_2 and δD_{H2} between Dec. 2001 and Jan. 2002.

* Indicates can or flask analyzed in duplicate.

† Date on which sub-samples from canisters were transferred to glass flasks.

♣ δD of H_2 reported as individual measurement, average of duplicate, or average of can/flask pair as appropriate.

♦ Δ_{dup} = difference between duplicate analyses of individual canisters or flasks.

♠ $\Delta_{c/f}$ = difference between δD of flasks and can pairs (average values used when can or flask analyzed in duplicate).

‡ H_2 concentration from mass spec peak integration.